Forgery-proof security element with color shift effect

The invention relates to forgery-proof security features, which exhibit a color shift effect caused by metal clusters which are separated by a defined transparent layer from a mirror layer.

WO 02/18155 discloses a method for the forgery-proof marking of objects, wherein the object is provided with a marking comprised of an electromagnetic wave-reflecting first layer, onto which a layer permeable to electromagnetic waves with a defined thickness is applied, whereupon onto this layer a third layer formed of metal clusters follows.

SUMMARY OF THE INVENTION

The aim of the invention is to provide a security feature with a color shift effect, wherein the security feature is to have additional security stages.

Subject matter of the invention is therefore a forgery-proof security feature comprising in each instance at least one layer reflecting electromagnetic waves, a polymeric spacer layer and a layer formed of metal clusters, characterized in that one or several of the layers, in addition to their function in the color shift effect setup, satisfy further security functions.

BRIEF DESCRIPTION OF THE DRAWINGS

In Fig. 1 to 6 examples of the security features according to the invention are depicted.

Therein indicate

1 the optically transparent carrier substrate,

2 the electromagnetic wave-reflecting first layer,

3 the polymeric spacer layer,

4 the layer built up of metal clusters,

5 an adhesion or lamination layer,

6 a protective (lacquer) layer,

7 a transfer lacquer layer,

8 a black layer,

10 the path of the rays of the incident and reflected light.

Fig. 1 illustrates a schematic cross sectional view of a first permanently visible marking on a sheet with double cluster setup,

Fig. 2 illustrates a schematic cross sectional view of a first permanently visible marking on a sheet with double cluster setup and the optic path of the optical detection means, for example spectrometer, color measuring device or the like,

Fig. 3 illustrates a direct double cluster setup with black background,

Fig. 4 illustrates an indirect double cluster setup with black background,

Fig. 5 illustrates a setup with partial reflection layer,

Fig. 6 illustrates a setup with a structured spacer layer of different thickness, and

Fig. 7 illustrates a system personalized by electromagnetic radiation.

DETAILED DESCRIPTION OF THE INVENTION

Carrier substrates 1 to be considered are preferably flexible sheets of synthetic materials, for example of PI, PP, MOPP, PE, PPS, PEEK, PEK, PEI, PSU, PAEK, LCP, PEN, PBT, PET, PA, PC, COC, POM, ABS or PVC. The substrate sheets preferably have a thickness of 5 - 700 μm, preferably 8 - 200 μm, and especially preferred a thickness of 12 - 50 μm. The sheets can be clear or matt-finished (in particular matt-imprinted). The scattering on matt sheets causes a marked change, in particular of the intensity in the color spectrum, such that a color code different than in clear sheets is generated.

Further, metal sheets, for example Al, Cu, Sn, Ni, Fe or special steel sheets having a thickness of 5 - 200 μm, preferably 10 - 80 μm, and especially preferred 20 - 50 μm, can also serve as the carrier substrate 1. The sheets can also be surface-treated, coated or laminated, for example with synthetic materials, or they can be lacquered.

Further, as carrier substrates can also be utilized cellulose-free or cellulose-containing paper, thermally activatable paper or composites with paper, for example composites with synthetic

materials with a grammage of 20 - 500 g/m^2, preferably 40 - 200 g/m^2.

The carrier substrate can also be provided with a release-capable transfer lacquer layer.

Onto the carrier substrate 1 is applied a layer reflecting electromagnetic waves 2. This layer 2 can preferably be comprised of metals, such as for example aluminum, gold, chromium, silver, copper, tin, platinum, nickel or tantalum, of semiconductors, such as for example silicon, and their alloys, for example nickel/chromium, copper/aluminum and the like or a printing ink with metal pigments. The electromagnetic wave-reflecting layer 2 can be applied over the entire surface or only partially using known methods, such as spraying, vapor deposition, sputtering, for example as printing ink, with known printing methods (gravure, flexographic, screen or digital printing), lacquer coating, roller spreading methods, slot eye, roll dip coating or curtain coating and the like.

For a partial application, a method utilizing a soluble color application for the production of the partial metallization is especially suitable. In this method in a first step a color application soluble in a solvent is applied onto the carrier substrate, in a second step this layer is optionally treated by means of an inline plasma, corona or flame process, and, in a third step, a layer of the metal or metal alloy to be structured is applied, whereupon in a fourth step the color application is removed by means of a solvent, optionally combined with mechanical action.
The soluble color application can be all-over or partial, and the application of the metal or of the metal alloy takes place over the entire surface or partially.
However, the partial electromagnetic wave-reflecting layer can also be produced employing a conventional known etching method.

The thickness of the electromagnetic wave-reflecting layer is preferably approximately 10 - 50 nm, however, greater or lesser layer thicknesses are also possible.
If metal sheets are utilized as the carrier substrate, the carrier substrate itself can already form the electromagnetic wave-reflecting layer.

The reflection of this layer for electromagnetic waves, in particular as a function of the thickness of the layer or of the metal sheet utilized, is preferably 10 - 100%.

The polymeric spacer layer 3 or the polymeric spacer layers succeeding thereon can also be applied over the entire surface or preferably partially.
The polymeric layers are for example comprised of conventional or radiation-curing, in particular UV-curing, color substance and lacquer systems based on nitrocellulose, epoxy, polyester, colophonium, acrylate, alkyd, melamine, PVA, PVC, isocyanate, urethane or PS copolymer systems.

This polymeric layer 3 serves essentially as a transparent spacer layer, however, depending on the composition, may in a certain spectral range be absorbing and/or fluorescing or phosphorescing. This property can optionally also be enhanced by adding a suitable chromophore. A suitable spectral range can be selected through the selection of different chromophores. Thereby, in addition to the shift effect, the polymeric layer can additionally also be made machine-readable. For example, in the blue spectral range (in the proximity of approximately 400 nm) a yellow AZO coloring agent can also be utilized, for example anilides, rodural or eosin. The coloring agent moreover changes the spectrum of the marking in a characteristic manner.

When using a fluorophore with excitation outside of the visible range (for example in the UV range) and irradiation in the visible range, with the choice of a suitable concentration, a marking can even be generated with color change on illumination. The layer structuring has optimally at the aimed for observation angle a spectrum with high absorption in the wavelength range of the emission of the fluorophore. Such a marking could further be readily combined with the UV test lamps at cash registers, which are already currently in use.

A further feasibility for generating a reversible color change comprises utilizing a switchable chromophore, such as for example bacteriorhodopsin. When illuminated with a suitable wavelength (bacteriorhodopsin between 450 mm and 650 mm) and sufficiently high intensity, such

chromophores change their absorption behavior. In the case of bacteriorhodopsin a structure change occurs which, after the illumination is switched off again, changes back to the starting state and switches the color of the chromophore between lilac and yellow. The integration of such chromophores into the layer system, for example the spacer layer, changes the absorption spectrum, with the switching behavior also occurring.

As a function of the quality of the adhesion on the carrier web or an optionally subjacent layer , this polymeric layer may show effects of decrosslinking, which leads to a characteristic macroscopic lateral structuring.
This structuring can be induced or specifically changed, for example through modification of the surface energy of the layers, for example through plasma treatment (in particular plasma functionalization), corona treatment, electron beam or ion beam treatment or through laser modification.
It is further possible to apply an adhesion promoter layer with regionally different surface energy.

The polymeric spacer layer 3 preferably has regions of different thickness. Through defined variation of the thickness (gradient, defined steps, defined structures) of the polymeric spacer layer a combination of different color shift effects is generated in a finished security feature (i.e., security element) (multicolor shift effect).

The thickness of the layer can therein be selectively varied within a wide range, for example in a range from 10 nm to 3 μm.

At a spacer layer thickness of more than approximately 3 μm the layer system no longer yields a color detectable by the human eye, but rather, depending on the mirror material, a somewhat darker metallic impression in comparison to the pure mirror. The reason is that the spectrum with increasing layer thickness becomes increasingly more complex (multipeak) and can no longer be resolved. However, for reading devices the spectrum continues to be well measurable and even highly characteristic, with the spacer layer thickness maximally to be measured depending on the

resolution capability of the particular device. This represents a feasibility for generating an inconspicuous but machine-readable marking.

Further, when applying the polymeric spacer layer a certain defined layer thickness course can be set either in one application step or by applying several layers, which, again can be all-over or partial depending on the desired layer thickness course.
The layer thickness course can also be implemented in the form of a stepped structure, wherein onto a base layer different thicknesses of a further polymeric layer are partially applied.
It is further feasible to apply several layers of different polymers, for example polymers with different indices of refraction.
In a special embodiment at least one layer of the polymeric spacer layer can be comprised of a piezoelectric polymer, wherein here electrical properties can be demonstrated either through direct contacting or through an electric field. As a function of the thickness or of the thickness course or of the layer thickness change of the spacer layer, a characteristic interaction with electrical or electromagnetic fields can also be demonstrated through simple optical evidence (for example with the naked eye, optical photometer and/or spectrometer).

In a special embodiment, at least one layer of the polymeric spacer layer may comprise optically active structures, for example diffraction gratings, diffraction structures, holograms and the like, which can be molded into the polymeric spacer layer, preferably before complete curing. A corresponding method is for example disclosed in EP-A 1352732 A or EP-A 1310381.

The polymeric spacer layer 3 is preferably applied by means of a printing method, for example by gravure printing. The fine structure in the spacer layer transferred from the impression cylinder or the printing plate forms in this case an additional forgery-proof feature. Depending on the printing die, the composition of the lacquer of the polymeric spacer layer and the production parameters, this fine structure forms a forensic and/or visible security feature which permits the unique assignment to the production process (finger print).
Further, several different layer thicknesses of the polymeric spacer layer can for example be

produced with a single cylinder. Due to the different thicknesses, different codes result. A further thickness region of the polymeric spacer layer is subsequently produced with a different cylinder, wherein optionally some codes may overlap. In the overlap region the same code can be produced with two different cylinders, whereby a further forensic and/or visible security feature is obtained and permits the unique assignment to the production process (finger print).
The additional finger print is utilized either as a forensic feature (third level feature) or as an additional code substructure.

Polymeric spacer layers are preferably also utilized which exhibit choleristic behavior. Apart from liquid crystal polymers, in which this behavior can be generated, polymers with two intrinsic chiral phases, such as for example nitrocellulose also exhibit this. Through the specific excitation of the rare second phase of chirality, for example through mechanical or electromagnetic energy application (thermal, radiative) or by means of catalysts, through wavelength-selective polarization an additional characteristic security feature is generated. The cholesteric behavior can therein lead to a characteristic change of the color spectrum, which can be detected by a reading device.

Onto the polymeric layer is subsequently applied an all-over or partial layer formed of metal clusters 4. The metal clusters 4 may be comprised for example of aluminum, gold, palladium, platinum, chromium, silver, copper, nickel, tantalum, tin and the like or their alloys, such as for example Au/Pd, Cu/Ni or Cr/Ni. Preferably cluster materials can also be applied, for example semiconducting elements of the principal groups III to VI or the auxiliary group II of the periodic system of the elements, whose plasmon excitation can be triggered (for example through X-ray or ion radiation or electromagnetic interactions). When viewing with a suitable reading device, a change in the color spectrum (for example an intensity change) or a blinking of the color shift effect becomes thereby visible.
The cluster layer 4 can also have additional properties, for example electrically conductive, magnetic or fluorescing properties. For example a cluster layer of Ni, Cr/Ni, Fe or core shell structures with these materials or mixtures of these materials with the above listed cluster materials have such additional features. Through core shell structures *inter alia* fluorescing clusters can also be

produced, for example by utilizing Quantum Dots® by Quantum Dot Corp.

The cluster layer 4 is applied all-over or partially, either precisely or partially congruent or offset with respect to the all-over or partial electromagnetic wave-reflecting layer.

The adhesion of the metal cluster 4 layer to the polymeric spacer layer 3 can preferably be adjusted with definition through the management of the application process of the cluster layer, such that at different adhesive strength evidence of manipulation through the destruction of the color effect is generated.

The lacquer of the spacer layer can also be set such that it has good adhesion to the metal (cluster, mirror) and not, however, to the base sheet. If this lacquer is printed over a partial Cu layer, the mirror layer is separated corresponding to the structuring of the cluster layer when detaching the element. Previously absolutely invisible evidence of manipulation is thereby formed.

This cluster layer 4 can be applied by sputtering (for example ion beam or magnetron) or vapor deposition (electron beam) or out of a solution, for example through adsorption.

In the production of the cluster layer in vacuum processes the growth of the clusters, and therewith their form as well as the optical properties, can advantageously be affected by setting the surface energy or the roughness of the subjacent layer. This changes in characteristic manner the spectra. This can take place, for example, through thermal treatment in the coating process or by preheating the substrate.
Further, these parameters can be selectively changed for example by treating the surface with oxidizing fluids, for example with Na hypochlorite or in a PVD or CVD process.

The cluster layer 4 can preferably be applied by means of sputtering. The properties of the layer, in particular the density and the structure, can therein be set especially through the power density, the quantity and composition of the gas utilized, the temperature of the substrate and the web transport

rate.

For the application by means of methods of printing technology, after an optionally necessary concentration of the clusters, small quantities of an inert polymer, for example PVA, polymethylmethacrylate, nitrocellulose, polyester or urethane systems, are added to the solution. The mixture can subsequently be applied onto the polymeric layer by means of a printing method, for example screen printing, flexographic or preferably gravure printing, by means of a coating method, for example lacquer application, spraying, roll coating techniques and the like.

The mass thickness of the cluster layer is preferably 2 - 20 nm, and especially preferred 3 - 10 nm.

In one embodiment, onto the carrier substrate a so-called double-cluster system can be applied, wherein on both sides of the spacer layer one cluster layer each is provided. Beneath the first cluster layer a preferably black layer 8 is applied. This black background can either be applied by means of a method using vacuum technology, for example as nonstoichiometric aluminum oxide or also as printing ink by means of a suitable printing method, and the printing ink can comprise additional functional features, for example magnetic, electrically conductive feature and the like. As the black or dark background can further also serve a correspondingly dyed sheet.

By placing a black sheet onto a double cluster setup a simple optical demonstration can be carried out on site (simple testing means). For example, a double cluster feature can be inserted as a viewing window into a bank note, credit card or the like. The optical demonstration of the presence of the double cluster feature takes place by placing onto it a black sheet, for example of polycarbonate.

The clusters on both sides of the spacer layer can be applied in different thicknesses, can each be structured or be applied all-over and/or in a system of different materials.
If, for example, a polymeric spacer layer is utilized with a defined layer thickness course or a step structuring the metal clusters are deposited preferably and directly at the steps or at specific sites of

the layer thickness course. This operation can be enhanced or diminished through suitable process management. For example, on microstructured surfaces different optical effects are generated than on smooth sheets. Thereby new (sub) codes result.

It is also possible to apply several layer sequences onto a carrier substrate, wherein, depending on the layout of the reflection layer (all-over or partial) and depending on the structuring of the spacer layers or layout of the cluster layer (all-over or partial, with register precision or overlapping with respect to the reflection layer) different color shift effects can be observed. For example, onto a reflection layer applied over the entire surface an optionally structured spacer layer can be applied, thereon a partial cluster layer, thereon, again, an optionally structured spacer layer, thereon, again, a preferably partial cluster layer, which is disposed so as to partially overlap the first cluster layer. Such sequences of spacer layer and cluster layer can usefully be repeated 2 to 3 times. Analogously, onto a partially applied reflection layer such systems can be applied, wherein here also, as a function of the layout of the partial reflection layer, again, different color shift effects are observed.

The layer system produced thus can subsequently be structured by means of electromagnetic radiation (for example light). Therein writing, letters, symbols, characters and signs, pictures, logos, codes, serial numbers and the like can be worked in for example by means of laser irradiation or laser gravure.
Through the appropriate selection of the radiative power either the layer system is partially destroyed or the thickness of the polymeric spacer layer is therein changed. The polymeric spacer layer usually swells in these regions, which generates a change of the color (peak shift to higher wavelengths). In contrast, the partial destruction brings about that the illuminated site either reflects metallically (separation of the electromagnetic wave-reflecting layer from the spacer layer) or that the material located behind the mirror becomes visible.
In this manner a specific structuring with colored, reflecting or colorless regions can be attained.

The illumination power can, however, be selected such that exclusively the color effect is changed, wherein partial regions are generated with defined different colors (multicolor shift effect). Essential

for the change is the energy actually absorbed by the layer system.

In a special embodiment, it is also possible to apply directly onto a carrier substrate, at least partially transparent in the visible spectral range, a cluster layer, onto this cluster layer subsequently, as described, a spacer layer and a further cluster layer is applied, wherein onto this cluster layer subsequently optionally a black layer, as already described, can be applied. Consequently, a so-called inverse layer system is obtained. (Fig. 4)

An inverse setup with a single cluster layer (application of the cluster layer onto the carrier substrate, subsequent application of the polymeric spacer layer and the electromagnetic wave-reflecting layer) can also be produced analogously, wherein the properties of the discrete layers correspond to the preceding description.

The carrier substrate can also already have one or several functional and/or decorative layers.

The functional layers can, for example, have certain electrical, magnetic, special chemical, physical and also optical properties.

To set electrical properties, for example conductivity, can be added for example graphite, carbon black, conductive organic or inorganic polymers, metal pigments (for example copper, aluminum, silver, gold, iron, chromium, lead and the like), metal alloys such as copper-zinc or copper-aluminum or their sulfides or oxides, or also amorphous or crystalline ceramic pigments such as ITO and the like. Further, doped or non-doped semiconductors such as for example silicon, germanium or ion conductors such as amorphous or crystalline metal oxides or metal sulfides can also be utilized as additives. Further, for setting the electrical properties of the layer can be utilized or added polar or partially polar compounds, such as tensides or nonpolar compounds such as silicon additives or hygroscopic or non-hygroscopic salts.

To set the magnetic properties paramagnetic, diamagnetic and also ferromagnetic substances such

as iron, nickel and cobalt or their compounds or salts (for example oxides or sulfides) can be utilized.

The optical properties of the layer can be affected by visible color substances or pigments, luminescent color substances or pigments, which fluoresce or phosphoresce in the visible, the UV or in the IR range, effect pigments, such as liquid crystals, pearlescent pigments, bronzes and/or heat-sensitive colors or pigments. These can be employed in all conceivable combinations. In addition, phosphorescent pigments alone or in combination with other color substances and/or pigments can be utilized.

Several different properties can also be combined by adding different additives from the list above. For example, it is possible to used dyed and/or conductive magnetic pigments. All of the listed conductive additives can be employed.
Specifically for dying magnetic pigments all known soluble and insoluble color substances or pigments can be utilized. For example, through the addition of metals a brown magnetic color can be adjusted to have a metallic, for example silvery, color tone.

Moreover, insulator layers, for example, can be applied. Suitable insulators are for example organic substances and their derivatives and compounds, for example color substance and lacquer systems, for example epoxy, polyester, colophonium, acrylate, alkyd, melamine, PVA, PVC, isocyanate, urethane systems, which can be radiation-curing, for example by thermal or UV radiation.

Into one of the layers can be worked forensic features, which permit testing in the laboratory or with suitable testing means on site (optionally while destroying the features), for example DNA in NC lacquer, antigenes in acrylate lacquer systems. DNA can, for example, be adsorbed or bound to the clusters. Isotopes can also be added to the clusters or in the mirror material or be present in the spacer layer (for example Elemental Tag by KeyMaster Technologies, Inc.). As the spacer layer can be utilized for example a deuterated polymer (for example PS-d) or as the mirror a mirror material having low radioactivity.

These layers can be applied with known methods, for example by vapor deposition, sputtering, printing (for example gravure, flexographic, screen or digital printing and the like), spraying, electroplating, roller coating methods and the like. The thickness of the functional layer is 0.001 to 50 μm, preferably 0.1 to 20 μm.

The coated sheet produced thus can optionally also be additionally protected by a protective lacquer layer 6 or be further finished by lamination or the like.

The product can optionally be provided with a sealable adhesive, for example a hot or cold seal adhesive, or a self-adhesion coating, applied onto the corresponding carrier material, or be embedded for example during the paper production for security papers through conventional methods.

The coated carrier materials produced according to the invention can be utilized as security features in bank notes, data media, security documents, labels, markers, seals, in packagings, textiles and the like.

EXAMPLES:

Example 1:

Onto a polyester sheet having a thickness of 23 μm a Cr cluster layer of thickness 3 nm is applied in a sputter process. Onto this cluster layer in gravure printing with a specially optimized impression cylinder a urethane lacquer is imprinted in a thickness of 0.5 μm as a polymeric spacer layer. Thereupon follows again the deposition of a Cr cluster layer in a thickness of 3 nm. In finishing, onto this cluster layer is laminated a sheet dyed black. A color shift effect from violet to gold is observed.

Example 2:

In the production of a thin-film system as in Example 1, portions of the layers are structured such that only with the register-precise superposition of a structured double cluster setup and a structured

black background sheet, the shift color with an underlayed moiré pattern becomes visible. For this purpose the polymer layer in the double cluster setup is structured in the manner of a chessboard, with the edge length of the chessboard fields molded to be smaller than 0.1 mm. The blackening of the background sheet is structured with analogous chessboard fields. With the register-precise superposition of the structured sheets the molding of the moiré pattern as well as also the shift color can be observed. In this manner, through simple on site testing highest security can be ensured.

Example 3:

In the production of a thin-film system as in Example 1, instead of the application of the second cluster layer through methods using vacuum technology, clusters are applied, which had been produced through chemical synthesis in solution and which are present as dispersion in solution. For this purpose such cluster-containing solutions are imprinted in very thin layers, or adsorbed out of the solution. If clusters are utilized, which additionally have further properties, additional security can be generated.

As powder-form cluster materials for imprinting, silver nanopowder by Argonide can be utilized.

As magnetic cluster materials can be utilized magnetic pigments by Sustech. Best suited are ferrofluids or pigments in power form of the type: FMA (super paramagnetic ferrite) with hydrophilic coating. FMA mean primary particle size: 10 nm diameter.

As core shell clusters can be utilized SSPH (Sequential Solution Phase Hydrolysis) particles by Nanodynamics or nanopowders can be utilized. For example Au on SnO_2 or Au on SiO_2 particles with an inner diameter of 20 nm and an outer diameter of 40 nm can be utilized. As fluorescing particles the particles by Quantum Dot Corporation can be utilized: as core material CdS and as shell material ZnS. Core diameter: 5 nm; shell diameter: 2.5 nm.

Example 4:

In an embodiment example an impression cylinder with different cell or well volumes in different regions over its width is produced. With this cylinder is imprinted onto a sheet covered with a uniform cluster layer the spacer layer. Due to the described implementation of the cylinder sharply delimited regions with defined different thicknesses of the spacer layer over the web width are

obtained. Subsequently a uniform mirror layer of aluminum is vapor deposited.
The bands with different color codes are subsequently separated in a slitting process. Thus, in one production run security elements with several different codes are produced.

Example 5:

From a sheet web produced as described in Example 4 a security strip is cut from the web such that a sharp code transition comes to lie precisely in the center of the strip. In this case the strip thus produced contains as additional security stage two machine- readable codes, which singly or jointly are detected with the reading device.

Example 6:

All of the described layer systems can be specifically and selectively structured by means of suitable lasers. In this example, by means of a 1064 nm Powerline laser by Rofin Sinar an inverse layer structure was partially destroyed at the lasered sites. The power was adjusted such that the laser causes the detachment of the polymeric spacer layer from the aluminum mirror layer, whereby the lasered sites no longer appear colored but rather show the metallic gloss of the mirror layer. The lasering is carried out selectively and punctiform. The depicted image is consequently composed of a dot matrix of metallically reflecting regions in the colored area. In this way, very rapidly (< 1 sec) individualized, forgery-proof markings, for example for identification passes, can be produced.

Example 7:

For the intrinsic marking of the layers described in the preceding examples marker substances can be utilized, which are only accessible to forensic proof. For this purpose, for example, to a nitrocellulose lacquer a marking of 1 per thousand solid DNA can be added to the lacquer volume. Under normal conditions (25°, 80% ambient humidity) the DNA adsorbs firmly on the nitrocellulose and is thus stably anchored in the lacquer matrix. By dissolving the lacquer layer or by extraction with boiling water, the DNA can be extracted in the laboratory and be demonstrated with methods utilizing molecular biology. By using suitable DNA sequences, these can also be demonstrated on site, for example through a suitable hybridization assay.